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(56) Documents cited

GB 1174922 GB 0850418
CA 80 145023w
CA 85 20726z

(58) Field of search

C2C

(54) Nitron compounds and stabilised rubber compositions containing them

(57) A C-substituted or unsubstituted aryl - N - substituted or unsubstituted (branched alkyl or cycloalkyl) nitron
having anti-fatigue and/or antiozonant properties in rubber.

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SPECIFICATION

Stabilised rubber compositions

- 5 This invention relates to stabilised rubber compositions; more particularly, this invention relates to additives which have static antiozonant properties when incorporated in organic rubbers; and to stabilised rubber compoundings and vulcanised rubber
- 10 incorporating these additives, possibly by chemical binding.

At the present time, the most successful class of antiozonant additive for rubbers comprises the *N*-aryl-substituted *p*-phenylene-diamines, notably the

15 *N*-aryl, *N'*-alkyl-substituted *p*-phenylene-diamines. The pre-eminent example is *N*-phenyl, *N'*-isopropyl-*p*-phenylenediamine (IPPD) commercially available as SANTOFLEX IP ("SANTOFLEX" is a registered Trade Mark of Monsanto Company). A major dis-

20 advantage of these additives is that, in service, a small fraction thereof becomes converted into an intensely coloured by-product which not only prevents their use in white or coloured rubber compositions but also prevents carbon black-containing

25 rubber compositions containing them being used contiguous with white or coloured polymer compositions into which the discoloration could migrate.

We accordingly, attempted to provide improved antiozonant additives (in which the tendency to

30 create discoloration in rubber compositions containing them was reduced) by preparing the analogous nitroxyls or hydroxylamines thereby obviating the presence of the free diamine which was believed to lead to the discoloring species. While many of the

35 novel additives prepared (especially 4,4'-dimethoxy diphenyl nitroxyl which, at 1% concentration, was more than twice as effective an antiozonant as IPPD) were highly efficient antiozonant additives, they too unfortunately caused discoloration. Indeed, there

40 appeared to be a direct relationship between the tendency to discolor and antiozonant activity in these additives.

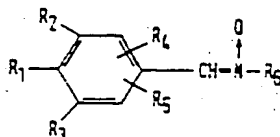
We have now prepared a novel class of additive which exhibits antiozonant activity in rubbers with a

45 reduced tendency to discoloration.

According, therefore, to one aspect of this invention we provide a *C*-substituted or unsubstituted aryl-*N*-substituted or unsubstituted (branched alkyl or cycloalkyl) nitroxyl having anti-fatigue and/or

50 antiozonant properties in rubber.

Particularly effective such compounds are those aldonitroxyls of the formula:



wherein:

R_1 represents a (+ I) or a (+ M) group;

- 55 R_2 and R_3 , which may be the same or different, each represent a substituted or unsubstituted (alkyl or alkoxy) group;

R_4 and R_5 , which may be the same or different, each

- represent a hydrogen atom or a substituted or unsubstituted (alkyl or alkoxy) group; and

R_6 represents a substituted or unsubstituted (branched alkyl or cycloalkyl) group.

- For example R_1 may represent an unsubstituted or alkyl substituted hydroxy group or an unsubstituted
- 65 or mono- or di-alkyl substituted amino group; or R_2 and R_3 , which may be the same or different, each represent an unsubstituted C_1 to C_3 alkyl or alkoxy group, preferably each represents an unsubstituted C_1 to C_4 alkyl group.

- 70 Examples of suitable substituents include a halogen atom, for example a fluorine, chlorine, bromine or iodine atom, a hydroxyl group, an alkoxy group, an alkyl carboxylic ester group, a mercapto group, a thioether group, a substituted or unsubstituted amino or amido group.

For ease of synthesis, it is preferred that R_2 and R_3 are the same. It is also preferred that at least one of R_4 and R_5 represents a hydrogen atom.

- R_6 may suitably be branched alkyl group, preferably a C_3 to C_6 branched alkyl group. It is particularly preferred that R_6 represents an isopropyl, sec. butyl or tert. butyl group.

This invention also provides the compound α -C-4-hydroxyphenyl-*N*-tert. butyl nitroxyl melting at 212°-

- 215°C; the compound α -C-4-hydroxy-3,5-dimethylphenyl-*N*-tert. butyl nitroxyl melting at 178°-180°C; the compound α -C-phenyl-*N*-tert. butyl nitroxyl melting at 75°-77°C; the compound α -C-4-hydroxy-3,5-dimethylphenyl-*N*-isopropyl nitroxyl melting at 192°-
- 90 195°C; α -C-4-methoxyphenyl-*N*-isopropyl nitroxyl (as a red, glassy solid); and the compound α -C-4-chlorophenyl-*N*-isopropyl nitroxyl melting at 183°-185°C.

The compounds of the invention may be prepared

95 in a variety of ways; for example:

- (a) by oxidation of the corresponding *C*-substituted or unsubstituted aryl-*N*-substituted or unsubstituted (branched alkyl or cycloalkyl) hydroxylamine;
- 100 (b) by reaction of a substituted or unsubstituted aryl ketone or aldehyde, especially an aldehyde, with a primary *N*-substituted or unsubstituted (branched alkyl or cycloalkyl) hydroxylamine (these materials are Schiff's bases);
- 105 (c) by *N*-alkylation of the corresponding oxime;
- (d) by reaction of the corresponding ketimine and primary hydroxylamine; and
- (e) by oxidation of the corresponding *N*-substituted imine.

- 110 Further details of these processes may be elucidated by analogy with those disclosed by Hammer et al in chem. Rev. 64, 474 (1964).

According to a further aspect of this invention, there is provided a compounding which comprises at

- 115 least one compound of the invention as herein described in intimate admixture with a rubber. The rubber may comprise natural rubber, polybutadiene, polyisoprene, chloroprene, butyl rubber, ABS, nitrile rubber, ethylene-propylene rubber, the toughening
- 120 phase in high-impact polystyrene or polyacrylonitrile.

The compound may comprise from 0.1 to 10, preferably, 0.5 to 6, especially 1 to 4 pph of the rubber.

In accordance with a preferred feature of this invention, the compound is chemically bound to the rubber, preferably by the method disclosed in UK 1503501. It is especially preferred to premill the additive, in the absence of oxygen, with the rubber.

In accordance with a particularly preferred feature of this invention there is provided a process for preparing a compounding as aforesaid, which process premilling a compound of the invention with the rubber for a time not exceeding 10 minutes, preferably not exceeding 6 minutes, particularly preferably not exceeding 2 minutes. Preferably the premilling is effected in the presence of oxygen. Where it is desired to utilise this feature with the abovementioned chemical it is necessary to effect the former procedure first.

This invention further provides a compounding prepared by this process.

This invention also provides a rubber compounding as herein described which has been vulcanised.

This invention provides a synergistic mixture of a nitrone of this invention and a rubber antioxidant.

The following Examples illustrate the invention.

EXAMPLE 1

3,5-Dimethyl-4-hydroxybenzaldehyde was synthesised by the formylation of 2,6-xynol according to the procedure described by Nikiforov *et al* (Bull. Acad. Sci. USSR div. Chem. Sci. p. 559 (1965)). 12.2 g (0.1 moles) of 2,6-xynol was used together with 35 g of boric acid, 25 g of hexamethylenetetraamine and 100 ml ethylene glycol. The yield was 10.5 g (70% of theoretical). Melting point: 110-113°C.

2-Methyl-2-nitropropane was prepared by the oxidation of tertiary butylamine using hydrogen peroxide according to the procedure described by Stowell (J. Org. Chem., 36, p. 3055 (1971)). 36.6 g (52 ml); (0.5 moles) of tertiary butylamine was used. The yield was 25.8 g (0.293 moles; 59% of theoretical). Boiling point 126-128°C.

The corresponding hydroxylamine was then synthesised by the reduction of the 2-methyl-2-nitropropane using zinc dust and ammonium chloride according to the method described by Greene *et al* (J. Org. Chem. 34, p. 2269 (1969)). 25 g (0.28 moles) of the 2-methyl-2-nitropropane was used. The yield was 18.2 g (0.204 moles; 73% of theoretical). Melting point: 50-62°C.

The nitrone α -C-4-hydroxy-3,5-dimethylphenyl-N-tert. butyl nitrone was synthesised by the condensation reaction of the aldehyde with the hydroxylamine. N-tertiarybutyl-hydroxylamine (3.0 g; 0.033 mole) and 3,5-dimethyl-4-hydroxybenzaldehyde (4.95 g; 0.033 mole) were dissolved in the minimum volume of absolute ethanol and allowed to stand at room temperature for a few days. Colourless crystals were formed. The crystals were separated by filtration and recrystallised from ethanol. Yield: 4.2 g (0.190 mole; 58% of theoretical). Melting point: 178-180°C.

Analytical data:

(i) calculated for $C_{13}H_{19}NO_2$			
element	C	H	N
expected	70.6	8.6	6.3
found	71.0	9.2	6.5

(ii) Mass spectroscopy:

Molecular ion at $m/e=221$.

(iii) Infrared analysis (KBr disc)

3100-3300 cm^{-1} (broad OH stretch); 1590 cm^{-1} (aromatic C-C stretch); 1570 cm^{-1} (C=N stretch); 1160 cm^{-1} (N-O stretch); disappearance of the carbonyl stretch of the parent aldehyde at 1680 cm^{-1} .

N.B. typical literature values C=N of nitrones appear at 1560-1580 cm^{-1} (84); and the N-O stretch appear at 1150-1270 cm^{-1} (84).

(iv) N.M.R. analysis: (in acetone d_6).

1.5 δ (S; 9H; N-Butyl protons); 2.2 δ (S; 6H; ring methyl protons); 7.5 δ (S; 1H; -CH=N(O)-); 8.0 δ (S; 2H; aromatic protons); S=singlet.

EXAMPLES 2 to 6

The following nitrones were prepared in essentially the same manner.

Example 2 α -C-4-hydroxyphenyl-N-tert. butyl nitrone. Yield: 30%; melting point; 212-215°C.

Example 3 α -C-phenyl-N-tert. butyl nitrone. Yield: 70; melting point; 75-77°C.

Examples 4 α -C-4-hydroxy-3,5-dimethylphenyl-N-isopropyl nitrone. Yield: 53%; melting point: 192-195°C.

Example 5 α -C-4-methoxyphenyl-N-isopropyl nitrone.

Example 6 α -C-4-chlorophenyl-N-isopropyl nitrone. Melting point; 183-185°C.

EXAMPLE 7

100 g of natural rubber (SMR, 10) was premilled on a two roll open mill for 2 minutes with 1 g of the nitrone of Example 1; and was then compounded, in order shown, with:

zinc oxide:	5.0 g
stearic acid:	3.0 g
sulphur:	2.5 g
CBS:	0.6 g

The initial Wallace Plasticity (Po) was next determined at 120°C using a Wallace Plastimeter.

The experimental run was repeated premilling for 4 minutes, and also for 6 minutes. In all cases the premilling and compounding time totalled 15 minutes.

The vulcanising, antifatigue and antiozonant properties are shown, and compared with those of a control and a sample comprising IPPD, in the following Tables. Referring to Table 3, the colour rating (arbitrary scale) of the sample containing the additive of Example 2, at 20% strain, was 2, compared with 8 for the control and IPPD samples at the same strain.

TABLE 1

ADDITIVE	CONCENTRATION (phr)	Po	SCORCH TIME (min ⁻¹)	MAXIMUM TORQUE (lbs) ⁻¹	PRE-MILLING (min)
Control	0	7	12.25	57.2	0
Ex. 1	1.0	7	10.0	65.0	2
Ex. 1	1.0	7	11.6	58.5	4
Ex. 1	1.0	7	12.0	57.75	6
Ex. 2	1.0	7	9.5	66.0	2
Ex. 2	1.0	7	11.0	60.0	4
Ex. 2	1.0	7	11.6	59.0	6
IPPD	1.0	7	11.5	59.0	0

TABLE 2

ADDITIVE	CONCENTRATION (phr)	FATIGUE LIFE 60% extension (maximum)			PRE-MILLING (min)
		NO. CYCLES TO BREAK $\times 10^{-2}$	NO. HOURS TO BREAK	IMPROVEMENT OVER CONTROL	
Control	0	1250	20.0	0	0
Ex. 1	1.0	1800	30	50	2
Ex. 1	1.0	2218	37	85	4
Ex. 1	1.0	2297	38	90	6
Ex. 2	1.0	6543	110	450	2
Ex. 2	1.0	6162	103	410	4
Ex. 2	1.0	5531	93	365	6
IPPD	1.0	16440	274	1270	0

TABLE 3

ADDITIVES		TIME OF OZONE EXPOSURE (hr)																	PRE-MILLING
Sub-scripts refer to strain (%)	CONC (phr)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	(min)	
Control ₁₀	0	0	0	1	4.5	5												0	
Control ₂₀	0	0	0	0	2	5												0	
Control ₃₀	0	0	0	0	0	0	1	2	3	5								0	
Ex. 2 ₁₀	1.0	0	0	0.25	0.25	0.25	0.5	2.5	4.0	5								2	
Ex. 2 ₂₀	1.0	0	0	0	0.5	0.5	0.5	0.5	2.5	3	3	4	5					2	
Ex. 2 ₃₀	1.0	0	0	0	0	0	0	0	0	0	0.5	0.5	1.5	3	3	3.5	5	2	
Ex. 2 ₁₀	1.0	0	0	0.25	0.25	0.25	0.5	2.5	4.0	5								4	
Ex. 2 ₂₀	1.0	0	0	0	0.5	0.5	1.5	2	3	3	3.5	5						4	
Ex. 2 ₃₀	1.0	0	0	0	0	0	0	0	0	0	0.5	0.5	2	3	3.5	4	5	4	
Ex. 2 ₁₀	1.0	0	0	0.25	0.25	0.25	3	5										6	
Ex. 2 ₂₀	1.0	0	0	0	0.5	0.5	2	2.5	3.5	5								6	
Ex. 2 ₃₀	1.0	0	0	0	0	0	0	0	0	0	1.5	3	3.5	3.5	4	4	5	6	
IPPD ₂₀	1.0			1					5										

Notation: 0: No cracks

1: Fine cracks (ca. 0.5 or 1.0 mm) visible under x5 magnification

2: Fine cracks (ca. 1 to 2 mm) visible to naked eye

3: Cracks 2 to 5 mm

4: Cracks penetrated specimen

5: Test piece broken

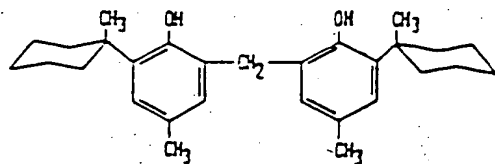
EXAMPLE 8

Example 7 was essentially repeated using the nitrene of Example 4. The maximum torque was 60 lbs⁻¹; the number of hours to break was 130; and the 5 time of ozone exposure to failure was 70 hours. The

colour rating was 3.

EXAMPLE 9

Example 7 was essentially repeated using the nitrene of Example 4 in admixture with 1 g of Nonox 10 WSP:



The antifatigue and static antioxidant results are shown in Table 4.

Table 4

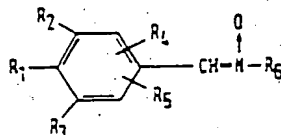
Additive	No. hours to break	No. hours to break (75 ppm ozone) 70% stain
Control	20	20
Monox USP	65	20
Nitrone Ex. 4	120	72
{ Monox USP Nitrone Ex. }	206	54

This Example illustrates the complementation effect of added thermal antioxidant: while this addition somewhat reduced the time of exposure to failure, it will be seen that it considerably enhanced the time to break.

CLAIMS

1. A C-substituted or unsubstituted aryl-N-substituted or unsubstituted (branched alkyl or cycloalkyl) nitron having anti-fatigue and/or antioxidant properties in rubber.

2. A compound according to Claim 1 of the formula:



15 wherein:

R₁ represents a (+ I) or a (+ M) group;

R₂ and R₃, which may be the same or different, each represent a substituted or unsubstituted (alkyl or alkoxy) group;

20 R₄ and R₅, which may be the same or different, each represent a hydrogen atom or a substituted or unsubstituted (alkyl or alkoxy) group; and

R₆ represents a substituted or unsubstituted (branched alkyl or cycloalkyl) group.

25 3. A compound according to Claim 1 or 2 wherein R₁ represents an unsubstituted or alkyl substituted hydroxy group or an unsubstituted or mono- or di-alkyl substituted amino group.

4. A compound according to any preceding claim wherein R₂ and R₃, which may be the same or different, each represent an unsubstituted C₁ to C₅ alkyl or alkoxy group.

5. A compound according to Claim 4 wherein R₂ and R₃, which may be the same or different, each represent an unsubstituted C₁ to C₄ alkyl group.

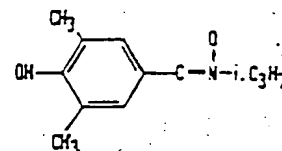
6. A compound according to any preceding claim wherein R₂ and R₃ are the same.

7. A compound according to any preceding claim wherein at least one of R₄ and R₅ represents a

40 hydrogen atom.

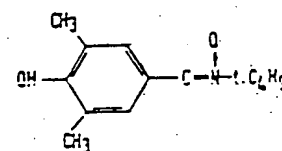
8. A compound according to any preceding claim wherein R₆ represents an isopropyl, sec. butyl or tert. butyl group.

9. The compound:



melting at 195°C.

45 10. The compound:



melting at 180°C.

11. A compound which comprises at least one compound according to any preceding claim in intimate admixture with a rubber.

12. A rubber compounding according to Claim 11 wherein the rubber comprises natural rubber, polybutadiene, polyisoprene, chloroprene, butyl rubber, ABS, nitrile rubber, ethylene-propylene rubber, the toughening phase in high-impact polystyrene or polyacrylonitrile.

13. A compounding according to Claim 11 or 12 wherein the nitron comprises from 0.1 to 10 pph of the rubber.

14. A compounding according to any of Claims 11 to 13 wherein the nitron is chemically bound to the rubber.

15. A process for preparing a compounding according to any of Claims 11 to 14 which process comprises premilling a compound according to any of Claims 1 to 10 with the rubber for a time not exceeding 10 minutes.

16. A compounding prepared by the process of Claim 15.

17. A rubber compounding according to any of Claims 11, 12, 13, 14 or 16 which has been vulcanised.

18. A mixture of a nitron according to any of Claims 1 to 10 and a rubber antioxidant.